# Solute Diffusion in Swollen Membranes. IV. Theories for Moderately Swollen Networks

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## Synopsis

A theoretical model was developed to describe solute transport through moderately swollen networks. The model is an extension of the previous analysis of Peppas and Reinhart (1983), and it describes the normalized effective diffusion coefficient of the solute through the network as a function of the equilibrium degree of swelling, $Q$, the hydrodynamic radius of the solute, $r_s$, the number average molecular weight between crosslinks, $\overline{M}_n$ and a function $f(\xi)$ of the mesh size $\xi$, which takes into consideration barriers due to crosslinks, entanglements, etc. For the development of this model, the Cohen–Turnbull (1958) free volume theory was modified to incorporate topological and mobility characteristics from de Gennes' analysis (1979).

## INTRODUCTION

### General

Transport across membranes has been studied for more than a century, but only recently has the technology of membrane separation processes at the molecular level been developed. The concept of molecular separation effected by permselective membranes has had an obvious appeal as a nondenaturing method of fractionation of proteins. Certain inherent advantages of membrane separation over conventional technologies are quite appealing: energy efficiency, pollution control, and biomedical applicability. Numerous biomedical and biochemical applications require membranes of separation purposes, due to very specific performance requirements coupled with the necessity of biological compatibility.

A variety of structural and morphological characteristics of the polymer affect solute diffusion through a membrane composed of a polymeric material. On the macroscale, thickness, pore structure (including size, size distribution, and type), laminations, or asymmetry of the membrane are found to influence mass transfer rates and selectivity. Other features become important on the microscale: fixed charges, dipoles, crystallinity, degree of swelling, degree of crosslinking, and thermodynamic transitions related to macromolecular relaxation phenomena (glassy/rubbery transitions in the presence of a solute and a swelling agent).

The term "heterogeneous membrane" has been used to indicate the internal physical structure and external physical and chemical performance of some membranes. From one standpoint, almost all membranes could be considered heterogeneous, despite the fact that, conventionally, membranes prepared from coherent gels have been called homogeneous. In this work

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it is assumed that within homogeneous membranes, there is neither macroscopic phase segregation of the polymeric and the nonpolymeric components nor heterogeneity in components, and therefore no macroscopic channels or pores. The main distinction between this homogeneous membrane concept, such as the analysis of Yasuda and Lamaze,[1] and the pore models of membrane behavior lies in the physical meaning of the pores. A pore model of membrane behavior assumes that fixed pores are present. In addition, the principles that apply to macroscopic phenomena are also assumed to apply to microscopic phenomena. This model leads to a calculated pore size of molecular dimensions, using Poiseuille's law, which may not have a realistic physical meaning.

The channels considered as pores in homogeneous membranes are not fixed in size or location. The geometry of the polymer network within the membrane sets the upper limit of the cross section of a penetrant molecule by limiting the size of the "pores." As a result of the plasticizing effect of any solvents present, sections of the macromolecules can exhibit a fairly high degree of mobility; the size and shape of the "pores" may thus be changing continuously.

## Effect of Polymer Structure on Solute Diffusion

The polymer medium has a considerable effect on solute diffusion. In essence, diffusion is controlled by the ease of forming enough free space in the membrane to enable the unit diffusion step to occur. In the free volume theory of diffusion,[2] this is discussed in terms of a probability of finding enough local free volume, while from the activation energy viewpoint, the process is discussed in terms of the energy needed to create the free space.[3] In both theories, the flexibility of the polymer chains and the cohesive energy of the polymeric structure are important as they relate to chain mobility.

The local segmental mobility (chain stiffness) is inherently affected by chain interactions arising from hydrogen bonding, polar group interactions, or simple van der Waals attractions among the components of the chains. As the number of these interactions per unit chain length increases, the segmental mobility, and therefore the rate of solute permeation, decrease. Any modification to the polymer chain structure which serves to change the segmental mobility changes the membrane permeability as a consequence.

A sufficiently high degree of crosslinking (dependent upon the penetrant size) will decrease the rate of permeation by affecting chain segmental mobility. In crosslinked polymeric networks, the macromolecular chains retain essentially their entire mobility, although junction fluctuations are hindered.[4] The more tightly crosslinked the network, the greater is the effect on the chain mobility. The crosslinking density $\rho_x$, the number average molecular weight between crosslinks, $\overline{M}_c$, and the mesh size $\xi$ are three interrelated structural parameters indicative of the amount of crosslinking present in the network. Of the three parameters, the mesh size $\xi$ may give the best indication of the structural screening effect of the membrane.

The decrease in chain mobility caused by increased crosslinking usually

has been found to increase the activation energy for diffusion, thereby decreasing the diffusion coefficient.[5] Both the increase in activation energy and the proportionate decrease in the diffusion coefficient become greater as the size of the diffusing molecule increases, suggesting that at high crosslinking densities there is a tendency for the diffusion medium to act as a molecular sieve in the same manner as inorganic zeolites.[6]

The mesh size of the polymeric network of a membrane, $\xi$, is the distance between crosslinks, both chemical and physical (e.g., chain entanglements). In this work, the mesh size is used almost interchangeably with the molecular weight between crosslinks. The exact relationship between these two parameters is developed. The mesh size, regardless of how it is expressed, is a measure of the effective area available for diffusion. This area determines the screening effect on solute diffusion, severly restricting the passage of very large molecules. As such, the mesh size will be stressed as a structural parameter of vital importance in the determination of the permeability of a polymeric membrane.

Numerous polymeric membranes are used in the crosslinked form. The polymer molecules are reacted at various points in their backbone chains to form a 3-dimensional network. Although this network is not souble in thermodynamically compatible liquids, it can be swollen by them. In all but highly swollen polymeric networks, chain overlapping can considerably alter the network structure, effectively resulting in a more highly crosslinked material. These chain entanglements act as physical crosslinks. The single most important structural parameter of the macromolecular network is the number average molecular weight between crosslinks, $\overline{M}_c$. When determined using swelling experiments, $\overline{M}_c$ refers to the distance between physical and chemical crosslinks, without differentiation.[7] The mesh size in loosely crosslinked, highly swollen membranes can be calculated by relating it to the molecular weight between crosslinks of a polymeric network using the same analysis as that provided by Flory[8] or with more advanced theories in the case of highly crosslinked networks.[9]

The number of studies investigating the effect of the crosslinking density of polymers on the solute diffusion coefficient is limited. This is mainly due to experimental difficulties in obtaining accurate values of the molecular weight between crosslinks.[10] Instead, most studies report some other parameter related to this molecular weight, e.g., the amount of crosslinking reagent added.[11] The importance of the crosslinking of the macromolecular chains has been recognized previously in providing a screening effect for solute diffusion. This structural parameter is almost always associated with the degree of swelling, degree of hydration, or an equivalent measure of the polymer volume fraction.[1,12]

## A NEW PHYSICAL MODEL FOR DIFFUSION IN MODERATELY SWOLLEN POLYMERS

### Diffusion in Swollen Networks

The theory for prediction of the screening effect of highly swollen membranes, developed elsewhere,[4] is modified to predict the screening effect of

moderately swollen membranes. The assumptions used to derive an expression for the diffusion coefficient include the following:

i. Diffusing molecules behave as ideal solutes.

ii. A certain fraction of the molecules present has the energy required for diffusion as a result of the normal fluctuations in the population's energy distribution.

iii. Local equilibrium exists between the activated molecules (those possessing the required energy) and the nonactivated molecules.

iv. No cooperative diffusion motions are present.

### Diffusivity from the Theory of Rate Processes

Diffusion can be modeled as a rate process including a transition state.[13] Considering the diffusion process on a reaction coordinate, the net flow of molecules moving in the forward direction per unit area per unit time, $v$, a mass velocity, can be expressed as

$$v = -\lambda^2 k \frac{dc}{dx} \tag{1}$$

where $dc/dx$ is the concentration gradient (negative since the concentration decreases in the direction of diffusion), $\lambda$ is the characteristic distance between successive equilibrium positions, and $k$ is the specific reaction rate for the diffusion equivalent to a characteristic frequency $\nu$. The diffusion coefficient is defined in terms of this net flow such that

$$D = \lambda^2 k \tag{2}$$

The parameters $\lambda$ and $k$ are functions of the structure and properties of the diffusing species and its environment, the diffusion medium.

The experimentally observed Arrhenius temperature dependence of the diffusion coefficient is an indication of the dependence of the characteristic frequency $\nu$ on temperature. This temperature dependence was recognized as an energetic effect[3]; the diffusion coefficient can thus be expressed in terms of an activation energy. According to the theory of absolute reaction rates, the specific rate constant for diffusion in one dimension, equivalent to the characteristic frequency $\nu$, is given by

$$\nu = \frac{kT}{h} \frac{F^*}{F^0} \exp\left(\frac{-e_0}{kT}\right) \tag{3}$$

where $F^*$ and $F^0$ are the partition functions of the system in the activated and normal states, respectively, $e_0$ is the activation energy per molecule at 0° K, and $kT/h$ is the universal frequency factor, its terms having their usual interpretations. The energetic term of eq. (3) may be related to $\Delta G^*$, the standard free energy change accompanying the formation of the activated state:

$$\nu = (kT/h) \exp(-\Delta G^*/RT) \tag{4}$$

From thermodynamics considerations, an alternate expression for the free energy change is possible, and the expression for the diffusion coefficient becomes

$$D = \lambda^2(kT/h)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \tag{5}$$

where $\Delta S^*$ and $\Delta H^*$ are the standard entropy and enthalpy changes accompanying the diffusion process.

## Derivation of the Screening Effect of Swollen Networks

To develop an expression for the screening effect of a swollen network (membrane), the expression derived for the diffusion coefficient of a solute in a solvent is extended to the three-component membrane systems.[1] The major assumption used in this extension is that the various components of the membrane are of a similar size on the molecular scale.[14] Using subscripts 1, 2, and 3 to indicate the solvent (usually water), solute, and polymer, and the subscript 13 to designate the swollen polymer membrane, the expression for the diffusion coefficient of a solute in a swollen polymer membrane is derived from eq. (5) in a manner similar to that followed by Yasuda et al.[15]:

$$D_{2,13} = \lambda_{2,13}^2\,(kT/h)\exp(\Delta S_{2,13}^*/R)\exp(-\Delta H_{2,13}^*/RT) \tag{6}$$

A similar expression can be written for the diffusion coefficient of the solute in the solvent only. The normalized diffusion coefficient, a ratio of the diffusion coefficient of the solute in the solvent-swollen membrane to the diffusion coefficient of the solute in the solvent only, gives a good indication of the screening effect of a membrane. For an isothermal system, the normalized diffusion coefficient can be written as

$$\frac{D_{2,13}}{D_{2,1}} = \frac{\lambda_{2,13}^2}{\lambda_{2,1}^2}\,\frac{\exp(\Delta S_{2,13}^*/R)}{\exp(\Delta S_{2,1}^*/R)} \tag{7}$$

An additional assumption made is that the membrane is swollen enough such that the enthalpic contributions to the diffusion coefficients cancel. This is reasonable since, in both cases, the diffusing species encounters an environment composed essentially of water. If the membrane is highly swollen (with equilibrium polymer volume fraction $v_3 \leq 0.10$), one could assume the jump lengths for diffusion would be approximately the same. The Peppas–Reinhart model[4] for solute diffusion in highly swollen makes this assumption. The jump length for diffusion in a membrane in any state other than the highly swollen is not the same as the jump length in a pure solvent.

## Extension of Theory to Moderately Swollen Membranes

A number of attempts have been made to explain the temperature dependence of the diffusion coefficient and the observed relationship between penetrant size and activation energy of diffusion. These attempts may be classified as either free volume or molecular theories. An example of the former is the hard sphere liquid model,[16] which is thermodynamic in nature,

i.e., the theory does not take into account the detailed molecular structure of the polymer–penetrant system. The basic idea behind the development of the free volume theory is that molecular transport occurs by the movement of molecules into voids, with a size greater than some critical value, formed by redistribution of the free volume. This free volume theory predicts a strong temperature dependence of the activation energy of diffusion above the glass transition temperature $T_g$, and has been successfully applied to the diffusion of complex molecules.

In this molecular theory, a cell model has been used to interpret the thermodynamic properties of the polymer chain molecules; expressions derived are based on the predictions of intermolecular and intramolecular interactions resulting from the model. The results concur only with diffusion of relatively simple molecules through polymers, as the activation energy is not predicted to be explicitly dependent on temperature. To analyze the expression for the normalized diffusion coefficient, both theoretical frameworks will be used: the free volume theory to analyze the entropic contribution of eq. (7) and the molecular theory to predict the jump length for diffusion.

### Determination of the Entropic Contribution

The free volume theory considers transport in a liquid consisting of hard spheres. The potential energy function which is obtained as a result of the model is constant except when there is intermolecular contact, when it is infinite. This function approximates the behavior of simple liquids rather well[16]; and any liquid bound by van der Waals forces would be adequately represented. Considering the swollen state of polymer membranes, a penetrant molecule can be thought of as diffusing essentially through the solvent phase; the free volume theory may thus be applied to a swollen membrane system.

The effect of the free volume of a system on diffusion is through the statistical redistribution of the free volume. Diffusing molecules move with a gas kinetic velocity but are confined to a "cage" bounded by immediately neighboring molecules. Random fluctuations in density occasionally open a hole within the cage large enough to permit a considerable displacement of the molecule within the cage. Successful diffusive transport occurs if another molecule fills the hole vacated by the first molecule before it can return to its original position. Diffusion is treated simply as translation of a molecule across a void within its cage, and does not occur as a result of an activation.

Using continuum mechanics, an expression for the average distribution of free volume, $p(v)$, for a system with no energy change upon redistribution can be obtained:

$$p(v) = \frac{\gamma}{v_f} \exp\left(-\frac{\gamma v}{v_f}\right) \tag{8}$$

where $v$ is the free volume, $v_f$ is the average free volume, and $\gamma$ is an overlapping factor, usually 1.0 (no overlap). Diffusion does not occur unless

the free volume $v_f$ exceeds a critical volume $v^*$, where $v^*$ is just large enough to permit another molecule to fill the void left by the displacement. The total probability of finding a hole of volume $v^*$ or larger is obtained from the distribution of probabilities through integration of eq. (8) within the appropriate limits:

$$p(v^*) = \int_{v^*}^{\infty} p(v)\, dv \tag{9}$$

The integral may be simplified:

$$p(v^*) = \exp(-\gamma v^*/v_f) \tag{10}$$

This equation for the probability of a free volume necessary for diffusion is valid for diffusion in a pure liquid only.

The free volume analysis is now applied to a polymeric membrane system. The entropy term in the normalized diffusion coefficient, eq. (7), results from two processes and the associated probabilities: (i) the conformational probability of forming a hole sufficiently large for the passage of the diffusing molecule; and (ii) the probability of finding in the membrane space for a hole of at least the same size as the diffusing molecule unhampered by the impermeable chain crosslinks of the membrane. As the first probability is analogous to that calculated in the free volume theory, the total probability may be expressed by imposing an additional proportionality factor onto eq. (10).

The Cohen–Turnbull free volume analysis[16] was modified by Fujita[2,17] in order to interpret diffusion in a two-component system of polymer and solvent. This modified version is set up as a correlative rather than a predictive theory and has provided a useful basis for describing the temperature and concentration dependence of the diffusion coefficient in different polymer-solvent systems.[18,19] Redefining $v_f$ as the average free volume of a membrane per unit volume of the membrane system (incorporating the overlap factor $\gamma$), the probability that a diffusing species of volume $v_d$ will encounter a membrane hole of volume $v_p$, where $v_p \geq v_d$, may be expressed as

$$p(v^*) = B(v_p) \exp(-v_d/v_f) \tag{11}$$

This function is the product of two probabilities describing the chance that the diffusing species of volume $v_d$ can find a "hole" in the membrane of size at least $v^*$, the effects of membrane and diffusing species size having been split. The term $B(v_p)$ is dependent primarily upon the size and shape of the polymer structure in the membrane formed by the chemical crosslinks and physical entanglements (i.e., the pore or mesh structure). The second term, $\exp(-v_d/v_f)$, is dependent upon the size and shape of the diffusing species as before.

The calculation of the entropic contributions to the normalized diffusion coefficient is straightforward using the well-known Boltzmann equation

$$\Delta S^* = R \ln p(v^*) \tag{12}$$

For diffusion of a solute of size $v_2$ in a polymeric membrane, the entropic contribution may be written as

$$\Delta S^*_{2,13}/R = \ln B(v^*_{13}) - v_2/V_{13} \tag{13}$$

where $v^*_{13}$ refers to a characteristic size of the holes present in the membrane and $V_{13}$ refers to the average free volume of the membrane. For diffusion of a solute in a solvent only, the entropic contribution may be written as

$$\Delta S^*_{2,1}/R = \ln B(v^*_1) - v_2/V_1 \tag{14}$$

where $v^*_1$ refers to a characteristic size of the holes present in the solvent and $V_1$ refers to the average free volume of the solvent. The proportionality factor $B(v^*)$ will be chosen such that $B(v^*_1)$ is identically equal to 1.0 as this term represents the effect of the presence of the membrane.

Upon substitution of the expression relating the entropic contributions to the probability of a void of a certain volume, eqs. (13) and (14), into the expression for the normalized diffusion coefficient of a membrane, eq. (7), one obtains the expression

$$\frac{D_{2,13}}{D_{2,1}} = \frac{\lambda^2_{2,13}}{\lambda^2_{2,1}} B(v^*_{13}) \exp\left[-v_2\left(\frac{1}{V_{13}} - \frac{1}{V_1}\right)\right] \tag{15}$$

## Determination of the Diffusional Jump Length

The jump length for diffusion in membranes may be predicted based on an analysis of concentrated polymer solutions.[20] It is assumed that the polymer, although noncrystalline, possesses regions where the chain bundles are parallel for short distances (of the order of several nanometers) such that these regions have an approximate semicrystalline order. X-ray diffraction results for various noncrystalline polymers show some order exists both parallel and perpendicular to the polymer chains; in addition, the small difference in density between a crystalline and a noncrystalline form of a polymer indicates that the average packing in each form cannot be much different.[21] Prediction of the jump length in swollen membranes is then based on a tube model representing the microstructure of a polymer.

For diffusion through a membrane structure consistent with the tube model proposed, the penetrant may move in two ways: (i) along the axis of the chain bundles (within a tube formed by the bundle) or (ii) perpendicular to the axis of the chain bundle (between two chains sufficiently separated).

During the course of normal thermal vibrations and rotations of the polymer segments, the chain bundle expands and contracts. The motion of the segments can coordinate in such a way as to produce a cylindrical void adjacent to the sorbed molecule. The presence of this void would allow penetrant movement parallel to the polymer chains. Since the oscillating movement of the polymer segments is likely to be slower than the translational rate of the penetrant molecule by an order of magnitude or more,[20] the void exists long enough, and this type of penetrant motion occurs rapidly enough such that the penetrant may make jumps of any length along the

axis of the chain bundle. This type of solute movement is halted whenever the molecule encounters a barrier at either end of its confining tube. After encountering such a barrier, the molecule may progress through the material only by moving via a separation of the polymer chains to an adjoining tube. This second process requires an activation energy equal to that needed to separate the chains just enough to accommodate the molecule. The penetrant moves a long distance within the tube formed by polymer chains before encountering a barrier large enough so that chain separation becomes a viable alternative.

The two processes, movement parallel and perpendicular to the polymer chains, occur effectively in series. As it is the energy of the shortest jump that determines the observed activation energy, the first process may be regarded as having a very small activation energy, effectively zero, while, for the second process, there is an activation energy equal to that necessary to produce a minimum chain separation that will accommodate the molecule. If the two processes occurred in parallel, the first would predominate due to energetic considerations, and no activation energy of any significance would be observed. As this is not the case, the processes would seem to occur in series, and the observed activation energy would be that of the second process, which is rate-limiting.

Although the jump length is not predictable within the limits of the present theory, a functional form is suggested by simple thermodynamic arguments. In analyzing the tube model for polymer–solvent system to predict the jump length, it is noted that the diffusional jump will be terminated by a barrier requiring more energy for penetration than that required for chain separation. Thus the jump length will be inversely proportional to the concentration of barriers of penetration energy $\Delta E$, assuming that the frequency of these barriers along the chains is a monotonically decreasing function of this energy. The barriers to diffusion parallel to a polymer chain bundle would include crystallites, permanent physical entanglements, and chemical crosslinks. In practice, all forms of the barriers will act as chain crosslinks and, therefore, will be treated as such.

As a result of these assumptions listed above, one may formulate an expression for the crosslinking density and, therefore, the jump length. The crosslinking density (or molar concentration of crosslinks) may be expressed as a function of the free energy of the crosslink, $\Delta G'$ (in relation to the well-ordered state), and the forming temperature of the polymer, $T_f$:

$$\rho_x \simeq \exp(-\Delta G'/RT_f) \tag{16}$$

As $T_f$ is usually well above the temperature range of the diffusion experiments, any physical entanglements are "locked in," i.e., permanent, as previously assumed. The diffusional jump length is inversely proportional to the concentration of entanglements of penetration energy $\Delta G'$, assuming that the frequency of entanglements along the chains is a monotonically decreasing function of this energy. The jump length then is given by the expression

$$\lambda = \lambda_0 \exp(\Delta G'/RT_f) \tag{17}$$

where $\lambda_0$ is a length that corresponds to the number of segments on one chain that are involved in an entanglement.

The crosslinking entropy $\Delta S'$ and internal energy $\Delta E'$ contributions to the free energy of the crosslink are assumed to be increasing functions of the crosslinking density. These quantities are also assumed, as a first approximation, to be proportional to each other; the proportionality is such that $\Delta E'$ dominates:

$$\Delta S' \simeq k_1 \Delta E' \tag{18}$$

As used in the previous expression, $k_1$ is a constant such that

$$k_1 T_f < 1 \tag{19}$$

The expression for the free energy of the crosslink may then be simplified to

$$\Delta G' = \Delta E'(1 - k_1 T_f) \tag{20}$$

An equivalent expression for the free energy of the crosslinks, introducing the dependence on the crosslinking density as indicated by the ratio of the number averages of the molecular weight between crosslinks, $\overline{M}_c$, to the molecular weight of the chains, $\overline{M}_n$, follows accordingly:

$$\Delta G' = \Delta E'(1 - \overline{M}_c/\overline{M}_n) \tag{21}$$

It is to be noted that the molecular weight ratio satisfies the requirement that the dimensionless constant in the expression is less than one.

Identifying $\Delta E'$ with the penetration energy $\Delta E$ and inserting of eq. (21) into eq. (17), we obtain the desired expression for the jump length:

$$\lambda = \lambda_0 \exp\left(\frac{\Delta E'}{RT_f}(1 - \overline{M}_c/\overline{M}_n)\right) \tag{22}$$

Upon rearrangement to stress the dependence on the molecular weight ratio by lumping some parameters into a constant $k_2$, eq. (22) gives the final form of the expression for the diffusional jump length in a swollen polymeric membrane system:

$$\lambda = \lambda_0 \exp[k_2(\overline{M}_c - \overline{M}_n)] \tag{23}$$

The solute jump length in the solvent alone will be of the order of $\lambda_0$, and will be considered to be equal to this quantity.

Then, using eq. (15) and the various expressions derived for the various parameters, the expression for the normalized diffusion coefficient in highly or moderately swollen crosslinked polymeric networks becomes

$$\frac{D_{2,13}}{D_{2,1}} = \exp[k_3(\overline{M}_c - \overline{M}_n)]B(v_{13}^*) \exp\left[-v_2\left(\frac{1}{V_{13}} - \frac{1}{V_1}\right)\right] \tag{24}$$

where $k_3$ is simply twice the constant $k_2$. Use of this expression adds complexity to the model in that the normalized diffusion coefficient is now directly dependent on the molecular weight between crosslinks, $\overline{M}_c$.

## ANALYSIS OF THE MODEL PARAMETERS

### Effect of Mesh Size of the Membrane

The effect of the mesh size of the polymeric membrane on the solute diffusion coefficient is expressed by the term representing the characteristic area available for permeation, $B(v_{13}^*)$ in eq. (15), in the physical model for solute diffusion presented.

A functional form of the parameter $B(v_{13}^*)$ has been proposed for highly swollen membranes,[4] considering the diffusion coefficient to diminish in proportion to the area available for diffusion. The probability $B(v_{13}^*)$ has been expressed then as a function of the volume fraction of mesh sizes larger than a critical mesh size $\xi$, which is a minimum for a specific penetrant below which there is effectively no diffusion. Expressing the volume of mesh in terms of a cross-sectional area, $\alpha_m$, and a characteristic length $l_m$ of the same magnitude as the diffusional jump length, $v_{13}^*$ may be written as

$$v_{13}^* = \alpha_m l_m \tag{25}$$

As the cross-sectional area of a mesh, the exposed area of an ideal tetrafunctional mesh, is proportional[22] to the square of the end-to-end distance $\mathbf{r}$, then $\alpha_m$ is proportional to the following quantities:

$$\alpha_m \propto \mathbf{r}^2 \propto nl^2 \propto \overline{M}_c \tag{26}$$

where $n$ is the number of links between crosslinks for chains of the structure —[C—C]$_n$— and $l$ is the bond length between adjacent carbon atoms. The number of links for vinyl polymers is defined by

$$n = 2\overline{M}_c/M_r \tag{27}$$

where $M_r$ is the molecular weight of the repeating unit. The upper limit of the mesh size for unobstructed diffusion is characterized by $\overline{M}_c = \overline{M}_n$, i.e., the absence of crosslinks. The lower limit of $\overline{M}_c$ of the network is the value of $\overline{M}^*_c$ corresponding to the mesh size below which no diffusion of a specific solute occurs. The probability $B(v_{13}^*)$ has then been written as a function of the molecular weight between crosslinks of the network and these limiting values for the molecular between crosslinks:

$$B(v_{13}^*) = f[(\overline{M}_c - \overline{M}_c^*)/(\overline{M}_n - \overline{M}_c^*)] \tag{28}$$

in which $\overline{M}_n > \overline{M}_c > \overline{M}_c^*$ To a first approximation in highly swollen membranes, the function is linear:

$$B(v_{13}^*) \simeq (\overline{M}_c - \overline{M}_c^*)/(\overline{M}_n - \overline{M}_c^*) \tag{29}$$

The parameter $\overline{M}_c^*$ can be obtained from experiment by a best fit of the data.

It must be noted that this expression for $B(v_{13}^*)$ was develeped for highly swollen, amorphous crosslinked systems. The functionality may be assumed to be linear only for such membranes, either loosely crosslinked or highly hydrophilic (if water is used as the solvent) or both. The normalized diffusion coefficient, as given by eq. (15) incorporating eq. (29), correlates well the experimental results of water-soluble solutes in highly hydrophilic membranes. Considerable deviation from the predicted values of the diffusion coefficient occurs, however, when this linear expression is used with membranes either highly crosslinked, which are usually poorly swollen, or poorly swollen because of poor compatibility with water. Poly(2-hydroxyethyl methacrylate) is an example of such a membrane (limited in its swelling ability in water for thermodynamic reasons), which is not adequately represented by this approach.

In order to more accurately predict the effect of the mesh size on the screening effect of a nonhighly swollen macromolecular network, the work of de Gennes was used.[23] The theoretical framework presented by de Gennes for the characterization of polymer solutions was applied to swollen polymeric membranes based on an analogy between dilute and concentrated polymer solutions and highly and poorly swollen polymeric membranes. The theory of Peppas and Reinhart[4] was redeveloped for nonhighly swollen and/or highly crosslinked systems using concepts from the scaling theories of polymer solutions as these theories apply to swollen polymeric networks.

An analysis of swollen polymeric networks based on an analogy between polymer solutions and swollen networks, analyzed according to de Gennes' simple intuitive approach, has been proposed to describe the swelling process in these networks.[24] The parallel between polymer solutions and polymeric networks is to be drawn with the following correspondence:dilute solutions–highly swollen membranes; semidilute solutions–moderately swollen membranes; concentrated solutions–poorly swollen membranes. The physical significance of the different concentration regions will now be discussed.

As the solvent is removed from a polymer solution, the intermolecular interactions gradually become more pronounced, and at a certain concentration $c^*$ the domains of the polymer molecules are in a state of permanent contact. The concentration at which this occurs depends on the geometrical shape and the extension of the polymer molecules, the flexibility of their backbone chains, the extent of mutual chain attraction, and the width of the molecular weight distribution.[24] Upon increase in concentration, the semidilute region is attained, and entanglements are formed. A further increase in the concentration to a certain $c^+$ results in homogeneous segment distribution over the available volume. In this regime a homogeneous network of physically entangled polymer molecules is developed in the

polymer solution. The concentrations $c^*$ and $c^+$ have been regarded as critical concentrations for the transitions from dilute to semidilute and semidilute to concentrated solution behavior, respectively.

## Polymer Solution Behavior

The value of the overlap concentration can be expected[23] to be comparable to the local concentration inside a single unperturbed polymer chain coil. In a good solvent, this implies that $c^*$ may be expressed as a function of the number of links in the polymer chain, $n$, and the bond length between two consecutive atoms in the backbone chain, $l$:

$$c^* \simeq l^{-3} n^{-4/5} \tag{30}$$

In terms of the polymer volume fraction, the corresponding threshold, $v_3^*$,may be defined in a similar manner:

$$v_3^* \simeq n^{-4/5} \tag{31}$$

The number of links in the macromolecular chain is directly proportional to the molecular weight of the polymer. Since the threshold concentration refers to the onset of chain overlap, i.e., formation of entanglements, then this molecular weight may be considered as the number average molecular weight between entanglements, $\overline{M}_e$. Substitution of the parameter into eq. (31) yields an expression for the threshold polymer volume fraction in terms of this molecular weight between entanglements:

$$v_3^* \simeq \overline{M}_e^{-4/5} \tag{32}$$

A decisive step toward the understanding of semidilute polymer solutions was the introduction of a screening length, the mesh size, and the "blob" model. The concept of the screening length for correlation was first introduced to describe concentrated polymer solutions.[25] A semidilute polymer solution containing a certain amount of chain overlap behaves in much the same manner as a network, even to the extent of exhibiting a certain average mesh size. This network, composed of physically entangled macromolecules, is visualized as a sequence of blobs of size $\xi$, with each blob occupying a volume proportional to $\xi^3$. The blob encompasses the portion of the polymer chain between two successive entanglements. Each blob acts as an individual unit with both hydrodynamic and excluded volume interactions.

The scaling form of $\xi$ in the semidilute region, i.e., $v_3^* << v_3 << 1$, in the presence of a good solvent is expressed as follows:

$$\xi(v_3) \simeq l\, v_3^{-3/4} \tag{33}$$

The mesh size decreases rapidly with concentration of the polymer in a good solvent.

## Polymer Network Behavior

A swollen polymeric gel consists of a crosslinked network of flexible macromolecular chains which may be thought of as closely packed coils sealed together by the crosslinks. This situation is reminiscent of the overlap threshold concentration in semidilute polymer solutions. The gel then automatically maintains a concentration proportional to the overlap threshold concentration $c^*$. Swollen gels obey simple scaling laws, based on the polymer concentration in the gels and hence on the threshold concentration (which are independent of the preparation conditions) as polymer solutions do. The gel can be visualized as a collection of adjacent "blobs,"each blob being associated with one chain, and having properties very similar to those of a solitary chain.

Inside one of the blobs which compose a swollen network, the polymer chain does not interact with other chains (from the definition of the mesh size). The number of monomers per blob is related to this mesh size. The membrane itself can be considered essentially as a closely packed system of blobs; thus correlations of the excluded volume type exist. Based on an expression derived for the threshold concentration in semidilute polymer solutions, the network concentration $c'$ may be expressd as

$$c' = k(\phi)c^* \tag{34}$$

where $k(\phi)$ is a constant, of order unity, dependent on the functionality $\phi$ of the crosslinks and on the preparation conditions. For most polymeric networks, the functionality $\phi$ is 3 or 4 because of the nature of the crosslinking reaction. This expression was derived for macromolecular networks in good solvents.

Various scaling laws which apply to polymer solutions may be used for networks because of the parallel drawn between polymer solutions and polymeric membranes. This polymer concentration $c'$ can be related to the mesh size in much the same way as the threshold concentration $c^*$ is proportional to the distance between physical entanglements. When the network is placed in the presence of a solvent, it is assumed that the swelling of the elementary chain of the network (between two adjacent crosslinks, i.e., within a blob) is the same as that of an equivalent chain between two entanglements in a semidilute solution. As a consequence of this, the equilibrium swelling conditions of the gel may be expressed:

$$v_{3,s} \simeq n^{-4/5} \tag{35}$$

In this case, $n$ refers to the number of links between entanglements or crosslinks and thus is proportional to the molecular weight between crosslinks, $\overline{M}_c$, which includes the effect of entanglements:

$$v_{3,s} \simeq \overline{M}_c^{-4/5} \tag{36}$$

The mesh size of the network would then be expected to obey the same scaling form as that hypothesized for semidilute solutions. It is proposed

therefore, on the basis of the similarity of moderately swollen membranes to semidilute polymer solutions, that the mesh size of such a swollen network be approximated as

$$\xi_p \simeq l\, v_{3,s}^{-3/4} \tag{37}$$

The mesh size so obtained would include the effect of any crosslink, physical entanglement, or chemical bond.

The parameter representing the characteristic area available for permeation in the expression for the normalized diffusion coefficient is a function of the mesh size:

$$B(v_{13}^*) = f(\xi_p) \tag{38}$$

Upon substitution of eq. (37), this parameter $B(v_{13}^*)$ is expressed in terms of the polymer concentration as follows:

$$B(v_{13}^*) = f(v_{3,s}^{-3/4}) \tag{39}$$

Various functional forms of this dependence could be proposed, but at this stage of the development of the physical model for the prediction of the solute diffusion coefficient, perhaps only the simplest, a linear relationship (in much the same way as a linear relationship was proposed for the dependence of the diffusion coefficient in highly swollen membranes on the molecular weight between crosslinks) or a quadratic dependence (indicative of the effect of the available area for diffusion, i.e., the square of the mesh size), could be justified.

### Effect of the Degree of Swelling

The effect of the degree of swelling of a polymeric network on the solute diffusion coefficient is expressed explicity by the free volume dependence of the effective diffusivity. In the expression for the normalized diffusion coefficient, eq. (15), both the free volume of the membrane and that of the pure diluent, $V_{13}$ and $V_1$, respectively, appear. The free volume of the membrane can be written in terms of its component free volumes by considering the free volumes to be additive:

$$V_{13} = (1 - v_{3,s})V_1 + v_{3,s}V_3 \tag{40}$$

where $v_{3,s}$ is the polymer volume fraction at isothermal swelling equilibrium and $V_3$ is the free volume of the polymer. From the expression for the normalized diffusion coefficient, eq. (15), the free volume contribution $\Phi(V)$ has been given as

$$\Phi(V) = \left[\frac{1}{V_{13}} - \frac{1}{V_1}\right] \tag{41}$$

This term may be expanded in terms of the solute and polymer free volumes

by replacing the term $V_{13}$ in light of the expression derived above for the free volume of the membrane. The term $\Phi(V)$ may then be written as

$$\Phi(V) = \frac{v_{3,s}(V_1 - V_3)}{(1 - v_{3,s})V_1^2 + v_{3,s}V_1V_3} \tag{42}$$

This expression for the free volume contribution to the normalized diffusion coefficient is for the general case.

### Highly Swollen Membranes

In highly swollen membranes, the free volume of the polymer may be assumed to be negligible in comparison to that of the swelling agent. For highly swollen membranes, it is common to assume that the solute transport occurs by diffusion through the solvent only.[15] This seems reasonable considering both the amount of solvent present and the relative penetration by the solute of the solvent in comparison to the macromolecular chains which are hindered in moving by pendant side chains, crosslinks, and the coiled nature of the backbone chain.

Applying the assumption just discussed by neglecting the free volume of the polymer, the free volume parameter $\Phi(V)$ may be written as

$$\Phi(V) = \frac{v_{3,s}}{V_1(1 - v_{3,s})} \tag{43}$$

By defining the swelling ratio $Q$ as the reciprocal of the polymer volume fraction at equilibrium, this term $\Phi(V)$ becomes

$$\Phi(V) = 1/V_1(Q - 1) \tag{44}$$

which expresses the exponential effect of the membrane swelling ration on the normalized diffusion coefficient.

### Moderately Swollen Membranes

At very low levels of swelling, the role of the solvent is to plasticize the polymer, (i.e., to facilitate segmental motion), rather than to provide a medium of transport.[26] As the solvent is typically smaller then the monomer unit and certainly much smaller than the polymer chains, it is expected that all the elements of the polymer chain would be in intimate contact with the solvent. The proximity of the solvent would be determined by the thermodynamic interactions between the solvent and polymer. In hydrogels, this interaction would be expected to maintain a molecular separation close to that exhibited between water molecules. The free volume of the membrane would be expected then to be a strong function of the solvent volume fraction at low solvent concentrations (while the "bound" water layer is formed) until the free volume decreases from that of the polymer only to approach that of the solvent.

The free volume contribution in such moderately swollen polymeric networks must be determined using eq. (42). No simplifications as those used

to derive eq. (43) may be applied in this case. In terms of the swelling ratio $Q$, the free volume contribution may be expressed as

$$\Phi(V) = \frac{V_1 - V_3}{(Q-1)V_1^2 + V_1V_3} \tag{45}$$

Values for the free volumes of the polymer and the solvent are calculated in a straightforward manner.

## Solute Size

The size of the diffusing solute is indicated by the term $v_2$ in the expression for the normalized diffusion coefficient. This parameter expresses the characteristic volume of a particular solute. In general, $v_2$ may be written in terms of a cross-sectional area, $\pi r_s^2$, and a length $l_s$, which is on the order of the transitional jump length, which are characteristic of the solute:

$$v_2 = \pi r_s^2 l_s \tag{46}$$

For low molecular weight compounds which are well represented by a spherical molecule, both $r_s$ and $l_s$ would refer to either the equivalent spherical radius $r_e$ or the Stokes hydrodynamic radius. For a high molecular weight compound, the evaluation of this parameter is more complicated. With proteins, it is assumed that $r$ would refer to the half-axis of revolution, $a$, and that $l$ would be represented by the equatorial axis, $2b$.

## Final Form of the Physical Model

Upon substitution of the various expressions into eq. (24) for the normalized diffusion coefficient in a moderately swollen polymeric network, the model takes its final form

$$\frac{D_{2,13}}{D_{2,1}} = f(v_{3,s}^{-3/4}) \exp[k_3(\overline{M}_c - \overline{M}_n) - \pi r_s^2 l_s \Phi(V)] \tag{47}$$

with

$$\Phi(V) = \frac{V_1 - V_3}{(Q-1)V_1^2 + V_1V_3} \tag{48}$$

and

$$k_3 = \frac{-2\Delta E}{\overline{M}_n R T_f} \tag{49}$$

If one knows the functional form of the dependence of the diffusion coefficient on the mesh size, this form of the normalized diffusion coefficient may be used to predict the influence of the mesh size, the degree of swelling, and the solute size on the screening effect of a polymeric membrane.

Experimental verification of this theory and evaluation of the function $f(v_{3,s}^{-3/4})$ is offered in the next contribution of this series.[27]

## CONCLUSIONS

This contribution offers a new model for diffusion of solutes through moderately swollen networks. The model incorporates topological and free volume characteristics of the network and offers a general expression which shows the dependence of the diffusion coefficient on the degree of swelling, the mesh size of the network, and the solute size.

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